SUMMARY

Poly(vinyl chloride) (PVC) is one of the most successful modern synthetic materials. Because of its unique physical nature, this versatile plastic can be combined with a variety of chemical additives and modifiers. Considering that processing occurs at temperatures between 150 – 200 °C the serious disadvantage of PVC is its low thermal stability. This obstacle has been overcome for a long time by the addition of stabilizing agents mostly containing heavy metals. Nowadays, the use of these materials is subject to a range of regulations. The PVC industry fully supports and is deeply involved in the process of assessing the risks of additives. This has led to a voluntary commitment called Vinyl 2010 to phase out among other things the heavy metal (especially cadmium and lead) containing stabilizers. Nevertheless, for some applications no suitable heavy metal-free alternatives are yet available.

Many studies on the degradation and stability of PVC showed that the reason for such poor thermal properties originates from the polymerization process. Allylic and tertiary chloride containing structures (so-called structural defects) are being formed by hydrogen abstractions of inter and intramolecular nature (comprehensively summarized in **Chapter 1**). Briefly, internal allylic structures are formed by inter or intramolecular abstraction of a methylene hydrogen from a monomer unit in a polymer chain by the growing macroradical. The resulting polymer radical undergoes a transfer reaction with monomer. Tertiary chlorine is only present on the branch point carbons of butyl and some of the long branches. Long branches result from the abstraction of the hydrogen atom a –CHCl– part of the polymer and subsequent propagation. When the hydrogen abstraction proceeds via 1–5 intramolecular process (backbiting), 2,4-dichloro butyl groups (*i.e.* butyl branches) are formed.

The chlorine atoms contained in these structures are prone to elimination, thereby converting them into initiation sites during the degradation process. An improvement in this aspect, *i.e.* suppressing of the above-mentioned side reactions, could thus lead to PVC with better inherent thermal stability and this would complement and enhance any positive results achieved in the research on heavy metal free stabilizers. This doctoral research deals with the modification of the suspension radical polymerization process with the purpose of improving the thermal stability of the resulting polymer.

Bulk and suspension vinyl chloride polymerization have a unique characteristic, which is polymerization in two phases: liquid monomeric phase and a gel-like phase called polymer-rich phase. In the case of suspension polymerization, the polymer is formed inside the droplets stabilized by surface-active compounds.

The influence of the composition of the polymer-rich phase on the microstructure of the resulting polymer has been studied in **Chapter 2** by examination of the conversion dependence of the number of different types of defect structures. The liquid monomer-

rich phase is consumed and the monomer has to diffuse to the polymer-rich phase from the vapor phase and suspension medium already above 60% conversion. However, the impact of these changes on the concentration of defect structures was observable at 25% higher monomer conversion. In other words, increase in the number of both branched and internal unsaturated structures accompanied by a sudden decrease in the stability of the polymer was observed just after 85% monomer conversion. From the experimental and theoretical evidence, it can be deduced that, above this so-called threshold-conversion, the polymer-rich phase becomes extremely dense, making the diffusion coefficient of the monomer much lower than in the monomer-rich phase. This causes substantial reductions in the propagation rate, thereby allowing the chain-transfer processes to compete more effectively. An increase in the number of methyl branches above 85% conversion was also observed. That could not be explained based on the generally accepted mechanism. Formation of these defects by termination of rearranged head-to-head radicals by combination with growing macroradicals was suggested.

Next to the processes occurring inside the monomer droplets, events taking place in the water phase might have strong impact on the quality of PVC made by a suspension process. In **Chapter 3**, the molecular weight dependence of the structural defects was examined in PVC polymers produced at various conversions. Low molecular weight material isolated from high conversion PVC showed a reduced concentration of chloroallylic end groups (unsaturated defects formed by Cl abstraction from a head-to-head radical, which previously underwent 1–2 chlorine shift) but a substantially enhanced concentration of branches. At very high conversions, when the polymer-rich phase contains very low amount of monomer, some of the short chains are probably formed and remain at the interface of the polymeric and aqueous phase. These conditions resemble closely the so-called subsaturation polymerization where increased number of branches and internal double bonds and decreased number of chloroallylic end groups have been reported. Based on the results presented in **Chapter 3** it appears that a greater proportion of the "subsaturation-like" low molecular weight material is formed in the late stages of the polymerization. Additional proof for that was the considerable improvement in the thermal stability measured after extraction of low molecular weight material from 96.4% conversion polymer, compared to only negligible differences in case of PVC of 23.7% conversion.

Analysis of the molecular weight dependence of the number of internal double bonds revealed the end group like characteristics of these defects. Quantum chemistry calculations showed the 1–5 hydrogen shift of 1–2 Cl shifted head-to-head radical as the most likely origin for these structures. This backbiting reaction seems to be stereoselective, with the isotactic conformation appearing to be more resistant. Efforts to improve the thermostability of PVC should thus be directed at minimizing intramolecular transfer reactions.

The importance of the polymerization in polymer-rich phase on the frequency of the side reactions was reinforced by the increase in the number of branches and unsaturations observed in polymers made in earlier formed and denser polymer-rich phase (**Chapter 4**). Such an effect was induced by addition of different types and amounts of precipitants for PVC to the polymerization mixture. When a precipitant acting as a chain transfer was used, the number of defect structures showed a decreasing tendency with the increasing amount of the additive. The strongest impact was observed for the number of internal unsaturations, but the number of branches decreased as well. However, the changes were not significant enough to cause improvements in the thermal stability. Analysis of fractions showed an increased formation of low molecular weight material in the water phase.

Increasing segmental mobility of the molecules present in polymer-rich phase by adding a good solvent for PVC (**Chapter 5**) rendered polymers of higher quality, *i.e.* less structure defects content and a better thermal stability, by decreasing the diffusion control of propagation.

In addition, the formation of poor quality low molecular weight polymer in the water phase was diminished, probably caused by easier entrance of these short chains to the polymer-rich phase.

Nevertheless, the decrease in the number of the defects was limited by the increased mobility of the polymer chains caused by the swelling of the polymer-rich phase by the solvent.

The mechanism of formation of internal unsaturations was altered too, removing the contribution of intermolecular reactions.

Combination of the effects of the increase in segmental mobility and interaction of PVC molecules with the additive was studied in **Chapter 6**. This was achieved by addition of a compound able to interrupt the attraction forces between nearby polymer molecules, lowering in this way T_g of the polymerization mixture. Ester and aromatic functional groups are known to form hydrogen bonds with atoms present in PVC molecules. Addition of plasticizer – a compound containing any of or both these functionalities – prior to the polymerization favored, just like a good solvent for PVC, the reactions susceptible to diffusion control, such as propagation, transfer to monomer, or intermolecular hydrogen abstractions. Less hindrance of the propagation was reflected, especially in a decrease in the number of defects having their origin in an intramolecular transfer such as internal unsaturations and butyl branches. Faster intermolecular hydrogen transfer – one of the steps in the formation of long branches – was compensated by increased polymerization rate leading to only a slight decrease in the content of these branches. The addition of a small amount of plasticizer was thus an effective way to diminish intramolecular side reactions. Nonetheless, the use of plasticizer for suppression

of the side reactions presented the same disadvantages, caused by the higher segmental mobility, as the addition of solvent.

Another way to decrease the frequency of the side reactions used in this research project was addition of solid compounds (not altering the mobility of the polymer chains) potentially able to form complex with the radical chain end (**Chapter 7**) or with the whole polymer molecule (**Chapter 8**).

Addition of peracetylated β-cyclodextrin (perBCD) – ester groups containing cyclic sugars– was explored (**Chapter 7**) with the purpose of physical prevention of backbiting and intermolecular transfer reactions by surrounding the growing polymer chain-end. The presence of large amounts of peracetylated β-cyclodextrin lowered the frequency of the side reactions of intra- and intermolecular nature, which was reflected in the decrease of corresponding structural defects and improved thermal stability. Due to the good solubility of perBCD in vinyl chloride and poor miscibility with PVC, the cyclodextrin derivative mostly influences the course of the reaction when dissolved in the monomer. The interactions with perBCD already influence the side reactions from the early stages of the polymerization and the action of perBCD is probably limited by phase separation at conversions at which the amount of monomer left is too low to maintain it in the solution. Moreover, pyrolysis products of this modified carbohydrate probably catalyze the unzipping, accelerating the dehydrochlorination rate of the PVC powder.

Highly effective protection against hydrogen abstractions, leading to necessity of a lower amount of additive, was attempted by addition of linear polymeric molecules containing functional groups able to interact with PVC chains (**Chapter 8**). Poly(methyl methacrylate) (PMMA) was chosen because it was proven not to negatively influence the dehydrochlorination process and/or mechanical properties. Moreover, methacrylates are frequently used as processing aids for PVC.

Even a low amount of PMMA added to the polymerization mixture restrained intra- and intermolecular side reactions, leading to improved thermal stability of the resulting polymers.

The miscibility of the additive with PVC enhanced somewhat the suppression of the side reactions, but was not crucial. PMMA affected substantially the events on the polymer – water interface leading to a changed morphology. PMMA lowered the surface tension of the initial monomer droplets causing their destabilization and aggregation. Larger particles with broader particle size distribution were formed because of this process. Smaller surface area of such particles probably affected the reactions at the polymer – water interface described in **Chapter 3**. Formation of less low molecular weight material of poor quality is expected at such conditions.

The processes at the water–polymer interface and the possibility of the improvement in the PVC quality by their modification are certainly worthy of further research as well as the investigation of the protection of PVC chains from hydrogen abstraction by

complexation with different compounds. Compounds from the family of additives used in PVC compounding are especially interesting alternatives from not only a scientific, but also an economic point of view.